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⑯ Applicant: **KAO CORPORATION**
14-10, Nihonbashi Kayaba-cho 1-chome
Chuo-ku
Tokyo (JP)

⑯ Inventor: **Kioki, Yuichi**
1293-7, Musota
Wakayama-shi,
Wakayama (JP)
Inventor: **Moriyama, Tadashi**
137-1-204, Enokihara
Wakayama-shi,
Wakayama (JP)
Inventor: **Ikeda, Chikako**
3-5, Tsuhada
Wakayama-shi,
Wakayama (JP)
Inventor: **Okamoto, Juri**
3-9, Sunayamaminami 1-chome
Wakayama-shi,
Wakayama (JP)
Inventor: **Tamura, Yoshinori**
No. 2-302, 1-1, Minato
Wakayama-shi,
Wakayama (JP)

⑯ Representative: **Hansen, Bernd, Dr.**
Dipl.-Chem. et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

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⑯ Germicidal-disinfectant detergent composition.

⑯ A germicidal-disinfectant detergent composition comprising (a) a cationic germicide, (b) a metal chelating agent and (c) at least one surfactant selected from anionic surfactants, nonionic surfactants and amphoteric surfactants is described. Excellent detergency and germicidal action are provided.

BACKGROUND OF THE INVENTIONField of the Invention:

5 The present invention relates to a germicidal-disinfectant detergent composition comprising a cationic germicide which provides sustained, high level antibacterial activity, excellent germicidal-disinfectant action, and excellent detergent action.

Description of the Background Art:

10 Cationic germicides generally have both a broad antibacterial spectrum and immediate effects, and are thus widely used in hospitals, etc. Germicidal-disinfectant detergents comprising a cationic germicide and a surfactant are known. However, such detergents suffer from the fact that anionic surfactants and other substances having a negative charge, such as proteins, when present greatly lower the activity of the 15 cationic germicide.

Prior art attempts at preventing this reduction in germicidal activity having included coating the cationic germicide with a high molecular weight nonionic surfactant or a pH-sensitive polymer, and adding the cationic germicide in excess. Unfortunately, the coating processes reduce the activity of the cationic germicide and the process making use of excess germicide is not preferable from an economic point of 20 view.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a germicidal-disinfectant detergent composition in 25 which the antibacterial activity of a cationic germicide contained therein is not lowered, even in the presence of a substance having a negative charge. Providing a germicidal-disinfectant composition having excellent detergency is also an object of the present invention.

The present inventors have discovered that when a metal chelating agent is used in combination with a composition obtained by mixing a cationic germicide and at least one of an anionic surfactant, a nonionic 30 surfactant and/or an amphoteric surfactant, a germicidal disinfectant detergent composition is obtained wherein the cationic germicide exhibits its inherent action without a lowering of its antibacterial activity even when anionic surfactants and/or negative-charge carrying species are present. Moreover, excellent detergency is provided, thus leading to completion of the present invention.

In one embodiment of the present invention, there is provided a germicidal-disinfectant detergent 35 composition comprising (a) a cationic germicide, (b) a metal chelating agent, preferably present in an amount of at least 0.5 mol per mol of the germicide and (c) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants and amphoteric surfactants.

In another embodiment of the present invention, there is provided a method for germicidal and 40 disinfectant cleaning, which comprises cleaning a contaminated substance with a composition comprising (a) a cationic germicide, (b) a metal chelating agent, preferably present in an amount of at least 0.5 mol per mol of the germicide and (c) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants and amphoteric surfactants.

The germicidal-disinfectant detergent composition of the present invention provides excellent anti-bacterial, antigermicidal, antiviral, etc. activity (hereinafter referred to as germicidal action or effect), wherein 45 the action of the cationic germicide is not lowered even in the presence of a substance having a negative charge, such as an anionic surfactant. The composition of the present invention is also excellent in its detergency. Therefore, the use of the germicidal-disinfectant detergent composition according to the present invention in the cleansing of the skin, etc. can bring about a greatly increased germicidal effect compared with conventional germicides.

50 The above and other objects, features and advantages of the present invention will be readily appreciated as the same becomes better understood from the preferred embodiments of the present invention, which will be described subsequently in detail, and from the appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

55 Components (a), (b) and (c) according to the invention germicidal-disinfectant composition and method are described below.

Examples of the component (a) cationic germicides useful in the practice of the present invention include cationic surfactant-type germicides such as benzethonium chloride, benzalkonium chloride, dialkyl-dimethylammonium halides, monoalkyltrimethylammonium halides and their variants having the counter ions thereof changed to other anions; biguanide type germicides such as chlorhexidine and chlorhexidine gluconate; amino acid surfactants such as alkyldiamino ethylglycines and alkylpolyamino ethylglycines; and the like. The cationic germicides carry a positive charge and are typically ion-paired with a counter anion so as to provide a neutral salt when in the solid phase. Other useful cationic germicides are described in the The Merck Index, Merck & Co., Inc., Rahway, N.J., 1989 incorporated herein by reference. Mixtures of cationic germicides can be used. The cationic germicides are preferably incorporated in the invention 10 composition in an amount of 0.1-10 wt.% (hereinafter indicated merely by "%"), particularly 0.5-5% based on the total weight of the composition.

No particular limitation is imposed on the component (b) metal chelating agent other than its functional capacity to chelate a metal ion. Examples of such chelating agents useful in the present invention include ethylenediaminetetraacetic acid, hydroxyethyl-ethylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid, nitrilotriacetic acid, triethylenetetramine hexaacetic acid, phosphonic acids, tripolyphosphoric acid, ethylene glycol-bis(2-aminoethyl ether)tetraacetic acid, citric acid, maleic acid, polyacrylic acid, isoamylene-maleic acid copolymers, silicic acid, gluconic acid, hydroxybenzylimidinoacetic acid, imidinoacetic acid, and salts of the said acids. Of these, ethylenediaminetetraacetic acid, hydroxyethyl-ethylenediaminetetraacetic acid, citric acid, tripolyphosphoric acid, and salts of the said acids are particularly preferred. Mixtures can be 20 used.

It is preferred that the metal chelating agent be present in an amount of at least 0.5 mol per mol of the cationic germicide (a). Generally, it is preferably incorporated in a proportion of 0.5-5 mol, more preferably 0.5-2 mol, most preferably 1-2 mol per mol of the germicide. If the proportion is lower than 0.5 mol, the effect of preventing the lowering of the antibacterial activity of the germicide in the presence of a negative 25 charge is not fully achieved. The metal chelating agent is preferably incorporated in the invention composition in a proportion of 0.05-5%, particularly 0.2-3% based on the total weight of the composition.

In certain shampoos and rinses, a chelating agent may be incorporated in addition to an anionic surfactant and a cationic surfactant. In such cases, however, the amount of chelating agent incorporated is extremely small, and even if a germicide was present, the antibacterial activity of the germicide would not 30 be protected from being reduced, unlike the case of the present invention.

Examples of the component (c) anionic surfactants useful in the present invention include salts of higher fatty acids preferably having 10-14 carbon atoms, salts of higher alcohol sulfates preferably having 10 - 18 carbon atoms, salts of higher alcohol sulfonic acids preferably having 10 - 18 carbon atoms, salts of sulfated fatty acids preferably having sulfated fatty acids preferably having 10 - 18 carbon atoms, salts of sulfonated fatty acids preferably having 35 10 - 18 carbon atoms, salts of higher alcohol phosphates the alcohol moiety of which preferably has 10-14 carbon atoms, salts of fatty acid ester sulfates preferably having 10 - 18 carbon atoms, salts of fatty acid ester sulfonates preferably having 10 - 18 carbon atoms, salts of higher alcohol ether sulfonates preferably having 10 - 18 carbon atoms, salts of higher alcohol ether substituted acetic acids the alcohol moiety of which preferably has 8-18 40 carbon atoms (number of mols of ethylene oxide added: 1-15), condensates of a fatty acid and an amino acid, salts of fatty acid amide alkylolated sulfates preferably having 10 - 18 carbon atoms, salts of fatty acid amide alkylated sulfonic acids preferably having 10 - 18 carbon atoms, salts of carboxymethyl-substituted ethoxylated fatty acid amides the acyl moiety of which preferably has 8-18 carbon atoms (number of mols of ethylene oxide added: 1-15), salts of sulfosuccinates, alkylbenzenesulfonates preferably having 8 - 18 45 carbon atoms, alkylphenol sulfonates preferably having 8 - 18 carbon atoms, alkylnaphthalenesulfonates preferably having 8 - 18 carbon atoms, alkylbenzimidazolesulfonates preferably having 10 - 18 carbon atoms, and the like. Preferred salts are the Na, K, TEA (Triethanolamine), NH₄⁺ salts. Mixtures can be used.

Examples of the component (c) nonionic surfactants useful in the present invention include polyoxyethylene alkyl ethers, polyoxyethylene alkylene ethers, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, alkyl polyglycosides preferably having 8 - 18 carbon atoms, sucrose fatty acid esters preferably having 8 - 18 carbon atoms, alkyl polyglycerol ethers, and the like. Mixtures can 50 be used.

Examples of the component (c) amphoteric surfactants useful in the present invention include alkyl-dimethylamino fatty acid betaines preferably having 8 - 18 carbon atoms, alkyltrimethylammonium oxides preferably having 8 - 18 carbon atoms, alkylcarboxymethylhydroxyethylimidazolium betaines preferably having 8 - 18 carbon atoms, and the like. Mixtures can be used.

Of these, an anionic surfactant alone (meaning one or a mixture thereof) or a combination of an anionic surfactant (one or a mixture) with a nonionic surfactant (one or a mixture) and/or an amphoteric surfactant

(one or a mixture) is preferred as component (c).

Of these surfactants, the salts of higher fatty acids, the salts of higher alcohol phosphates, the salts of higher alcohol ether-substituted acetic acids, salts of carboxymethyl-substituted ethoxylated fatty acid amides, the alkyl polyglycosides, the alkyldimethylamino fatty acid betaines and the alkyldimethylamine oxides are particularly preferred. The Na, K, TEA(Triethanolamine), NH₄⁺ salts are preferred. To the extent 5 that there is any overlap between components (a) and (c), component (c) is at least one surfactant different from the material described in component (a) selected from the group consisting of anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof.

In order to provide the desired detergent effect, component (c), preferably an anionic surfactant alone or 10 a combination of an anionic surfactant with a nonionic surfactant and/or an amphoteric surfactant, is preferably incorporated in the invention composition in an amount of 1-80%, particularly 5-50% based on the total weight of the composition. When mixtures of anionic and nonionic surfactants are used, the anionic surfactant is preferably present in from 1 to 70 %, and the nonionic surfactant is present in from 1 to 70 % based on the total wt% of the component (c) surfactant. When anionic, nonionic and amphoteric surfactants 15 are all present, the preferred amounts are 1 to 70 , 1 to 70 , and 1 to 70 , respectively based on the total wt% of the component (c) surfactant.

In the germicidal-disinfectant detergent composition according to the present invention, the antibacterial, antiviral, etc. activity of the cationic germicide is not at all, or not significantly reduced even in the presence 20 of a substance having a negative charge, such as an anionic surfactant, because the cationic germicide is present in combination with a metal chelating agent. Therefore, it is also possible to incorporate an additional anionic polymer and/or the like into the germicidal-disinfectant detergent composition of the present invention. Examples of such anionic polymers include polymers having carboxyl groups, sulfonyl groups, sulfate residues or the like, for example, salts of poly(meth)acrylic acid, salts of polyvinyl alcohol sulfate, naphthalenesulfonic acid-formalin condensates or alkylene oxide adducts thereof.

25 In the germicidal-disinfectant detergent composition according to the present invention other additives, for example, salts, viscosity builders, germicides other than those described above, viscosity depressants, solvents such as ethanol and propylene glycol, perfume bases, colorants, etc. may be suitably incorporated within conventional limits not impeding the effects of the present invention, as needed.

The germicidal-disinfectant detergent composition according to the present invention can be prepared 30 by any method known per se in the art; for example, by mixing and/or stirring the individual components, and may be provided in various forms such as aqueous solution, solid, aqueous suspension, and the like.

The germicidal-disinfectant detergent composition according to the present invention can be applied to 35 surfaces, etc. with the object of germicidal and disinfectant cleaning; for example, handwashes, face cleansers, body shampoos, hair shampoos, laundry detergents and instrument-cleaning detergents in fields associated with medical care, food and environmental sanitation.

While not wishing to be bound by a particular theory, the present inventors believe a clue to the theory 40 of operation of the invention is discernable from the ¹³C-NMR chemical shift of the α -carbon of a fatty acid salt (which is an example of a present invention anionic surfactant): it is shifted to higher magnetic field in the presence of a cationic germicide. Therefore, it is believed that these substances undergo some interaction with each other. When EDTA (which is an example of a present invention metal chelating agent) 45 is present in or added to the above mixture, the ¹³C-NMR chemical shift of the α -carbon is returned to a lower magnetic field. It is therefore considered that the addition of the metal chelating agent prevents the reduction of the germicidal activity of the cationic germicide by eliminating or reducing the association of the metal chelating agent with the cationic germicide, and the like, so that the cationic germicide is returned to its original uninhibited state, thereby allowing its inherent action to be exhibited.

The present invention will hereinafter be described in detail by the following examples. However, it should be borne in mind that this invention is not limited to or by these examples.

Example 1:

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The germicidal effects of various germicides (benzalkonium hexadecylphosphate, benzalkonium chloride, didecyl- dimethylammonium chloride and chlorhexidine gluconate) both in the presence of an anionic surfactant and in the presence of a metal chelating agent added to a mixture of germicide and anionic surfactant were investigated.

Method

5 Triethanolamine laurate was used as the anionic surfactant and was mixed in a proportion of 28.35 parts by weight with 1 part by weight of each of the various germicides listed above, and to portions of the resultant mixtures was separately added sodium EDTA as the metal chelating agent in varied proportions of from 0.5-10.0 mols per mol of the germicide. Sterilized distilled water was added to each of the resulting mixtures to provide compositions having 100 parts by weight in total. As controls, systems to which the metal chelating agent, triethanolamine laurate or germicide was not added, and individual systems of these components, were prepared.

10 A germicidal test was performed in the following manner. Diluted systems of each mixture described above were prepared to inoculate each of germs (Escherichia coli IFO 3972 and Pseudomonas aeruginosa IFO 12689) to be tested to determine the concentration of the germicide at which the germs were completely killed, and the time required to completely kill the germs. More specifically, 0.1 ml of an SCD medium (product of Nippon Seiyaku K.K.) containing precultured germs (about 10^9 - 10^{10} cells/ml) was taken 15 out and inoculated in 10 ml of the systems described above diluted to predetermined concentrations (germicide concentration: 1, 5, 10, 25, 50, 75, 100, 200, 300 or 500 ppm) to conduct the test at room temperature. When predetermined periods of time (5, 10, 15 and 30 minutes) elapsed a portion of the system inoculated with the germs was taken out with a platinum loop and inoculated in a micro Petri dish (96-cell wells, product of CORNING Co.) containing 0.3 ml of an SCD medium for after culture. Culture was 20 conducted for 3 days at 30°C to determine the growth of germs (observation by the naked eye). Among these micro Petri dishes, the number of dishes where germs have been completely killed are defined as the number of sterilized areas (40 areas in the maximum number). The judgement of the efficacy of the tested solution was made by counting the sterilized areas.

The results are shown in Tables 1 and 2.

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Table 1

| Germicide | Amount added (part by weight) | Amount of triethanol- amine laurate (part by weight) | Amount of chelating agent added (mol) | Effect on <i>E. coli</i> (number of sterilized areas) | Effect on <i>P. aeruginosa</i> (number of sterilized areas) |
|---------------------------------|----------------------------------|--|---|---|---|
| Benzalkonium hexa-decyphosphate | 1.0 | 28.35 | 0.5 | 35 | 33 |
| | 1.0 | 28.35 | 1.0 | 35 | 34 |
| | 1.0 | 28.35 | 2.0 | 35 | 34 |
| | 1.0 | 28.35 | 5.0 | 35 | 33 |
| | 1.0 | 28.35 | 10.0 | 35 | 33 |
| | 1.0 | 28.35 | 0 | 2 | 1 |
| | 1.0 | 0 | 1.0 | 35 | 34 |
| | 1.0 | 0 | 0 | 34 | 34 |
| | 0 | 28.35 | 1.0 | 2 | 1 |
| | 0 | 28.35 | 0 | 2 | 1 |
| Benzalkonium chloride | 1.0 | 28.35 | 0.5 | 35 | 34 |
| | 1.0 | 28.35 | 1.0 | 36 | 34 |
| | 1.0 | 28.35 | 2.0 | 36 | 35 |
| | 1.0 | 28.35 | 5.0 | 35 | 35 |
| | 1.0 | 28.35 | 10.0 | 34 | 34 |
| | 1.0 | 28.35 | 0 | 2 | 1 |
| | 1.0 | 0 | 1.0 | 36 | 34 |
| | 1.0 | 0 | 0 | 34 | 33 |
| | 0 | 28.35 | 1.0 | 1 | 1 |
| | 0 | 28.35 | 0 | 0 | 1 |

Table 2

| Germicide | Amount added (part by weight) | Amount of triethanol- amine laurate (part by weight) | Amount of chelating agent added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|---|----------------------------------|--|--|--|---|
| Didodecyldimethyl- ammonium chloride | 1.0 | 28.35 | 0.5 | 37 | 36 |
| | 1.0 | 28.35 | 1.0 | 38 | 37 |
| | 1.0 | 28.35 | 2.0 | 38 | 37 |
| | 1.0 | 28.35 | 5.0 | 39 | 37 |
| | 1.0 | 28.35 | 10.0 | 36 | 35 |
| | 1.0 | 28.35 | 0 | 3 | 2 |
| | 1.0 | 0 | 1.0 | 37 | 34 |
| | 1.0 | 0 | 0 | 38 | 36 |
| | 0 | 28.35 | 1.0 | 1 | 1 |
| | 0 | 28.35 | 0 | 1 | 0 |
| Chlorhexidine gluconate | 1.0 | 28.35 | 0.5 | 38 | 30 |
| | 1.0 | 28.35 | 1.0 | 32 | 31 |
| | 1.0 | 28.35 | 2.0 | 32 | 31 |
| | 1.0 | 28.35 | 5.0 | 31 | 31 |
| | 1.0 | 28.35 | 10.0 | 30 | 30 |
| | 1.0 | 28.35 | 0 | 2 | 1 |
| | 1.0 | 0 | 1.0 | 34 | 32 |
| | 1.0 | 0 | 0 | 33 | 31 |
| | 0 | 28.35 | 1.0 | 1 | 1 |
| | 0 | 28.35 | 0 | 0 | 0 |

As apparent from Tables 1 and 2, it was confirmed that the germicidal action of the cationic germicides
55 is markedly hindered by the addition of the anionic surfactant, but is recovered by adding, to these
systems, a metal chelating agent in a proportion of 0.5-10 mol per mol of the cationic germicide.

Example 2:

Germicidal effects of various germicides (benzalkonium hexadecylphosphate and benzalkonium chloride) both in the presence of an anionic surfactant (triethanolamine laurate) and in the case where sodium citrate or sodium tripolyphosphate (metal chelating agents) was added to such a mixture were investigated.
5 A germicidal test was performed in the same manner as in Example 1. As a result, and as shown in Tables 3 and 4, the germicidal action of the cationic germicides is markedly hindered by the addition of the anionic surfactant, but is recovered by adding, to these systems, sodium citrate or sodium tripolyphosphate in a proportion of 0.5-10 mols per mol of the cationic germicide.

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Table 3

| Germicide | Amount added (part by weight) | Amount of triethanol- amine laurate added (part by weight) | Amount of sodium citrate added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|---------------------------------|----------------------------------|---|---|---|---|
| Benzalkonium hexa-decyphosphate | 1.0 | 28.35 | 0.5 | 31 | 29 |
| | 1.0 | 28.35 | 1.0 | 32 | 29 |
| | 1.0 | 28.35 | 2.0 | 32 | 31 |
| | 1.0 | 28.35 | 5.0 | 31 | 31 |
| | 1.0 | 28.35 | 10.0 | 30 | 28 |
| | 1.0 | 0 | 0 | 1 | 1 |
| | 1.0 | 0 | 1.0 | 35 | 34 |
| | 1.0 | 0 | 0 | 35 | 34 |
| | | | | | |
| | | | | | |
| Benzalkonium chloride | 1.0 | 28.35 | 0.5 | 32 | 30 |
| | 1.0 | 28.35 | 1.0 | 33 | 31 |
| | 1.0 | 28.35 | 2.0 | 33 | 31 |
| | 1.0 | 28.35 | 5.0 | 34 | 31 |
| | 1.0 | 28.35 | 10.0 | 31 | 30 |
| | 1.0 | 28.35 | 0 | 2 | 1 |
| | 1.0 | 0 | 1.0 | 36 | 34 |
| | 1.0 | 0 | 0 | 34 | 33 |
| | | | | | |
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Table 4

| Germicide | Amount added (part by weight) | Amount of triethanol- amine laurate (part by weight) | Amount of sodium tripolyphosphate added (mol.) | Effect on <i>E. coli</i> (number of sterilized areas) | Effect on <i>P. aeruginosa</i> (number of sterilized areas) |
|--------------------------------------|----------------------------------|--|---|---|---|
| Benzalkonium hexa- decylphosphate | 1.0 | 28.35 | 0.5 | 29 | 28 |
| | 1.0 | 28.35 | 1.0 | 30 | 29 |
| | 1.0 | 28.35 | 2.0 | 30 | 30 |
| | 1.0 | 28.35 | 5.0 | 31 | 30 |
| | 1.0 | 28.35 | 10.0 | 30 | 29 |
| | 1.0 | 28.35 | 0 | 1 | 1 |
| | 1.0 | 0 | 1.0 | 35 | 34 |
| | 1.0 | 0 | 0 | 35 | 34 |
| | | | | | |
| | | | | | |
| Benzalkonium chloride | 1.0 | 28.35 | 0.5 | 30 | 29 |
| | 1.0 | 28.35 | 1.0 | 31 | 29 |
| | 1.0 | 28.35 | 2.0 | 31 | 30 |
| | 1.0 | 28.35 | 5.0 | 31 | 31 |
| | 1.0 | 28.35 | 10.0 | 30 | 30 |
| | 1.0 | 28.35 | 0 | 1 | 1 |
| | 1.0 | 0 | 1.0 | 36 | 34 |
| | 1.0 | 0 | 0 | 34 | 33 |
| | | | | | |
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Example 3:

Germicidal effects of various germicides (benzalkonium hexadecylphosphate and benzalkonium chloride) both in the presence of an anionic surfactant and in the case where an ethylenediaminetetraacetate (dipotassium or disodium salt) as a metal chelating agent was added to such a mixture were investigated. A

germicidal test was performed in the same manner as in Example 1. The results are shown in Tables 5 and 6.

Table 5

| Germicide | Amount added (part by weight) | Amount of sodium polyoxyethylene (3.0) lauryl ether sulfate added (part by weight) | Amount of dipota- assium ethylenedi- aminetetraacetate added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|--------------------------------------|----------------------------------|---|---|--|---|
| Benzalkonium hexa- decylphosphate | 1.0 | 15.0 | 0.5 | 31 | 29 |
| | 1.0 | 15.0 | 1.0 | 33 | 30 |
| | 1.0 | 15.0 | 2.0 | 34 | 31 |
| | 1.0 | 15.0 | 5.0 | 33 | 31 |
| | 1.0 | 15.0 | 10.0 | 33 | 30 |
| | 1.0 | 15.0 | 0 | 3 | 4 |
| | 1.0 | 15.0 | | | 1 |
| Benzalkonium chloride | 1.0 | 15.0 | 0.5 | 30 | 29 |
| | 1.0 | 15.0 | 1.0 | 31 | 30 |
| | 1.0 | 15.0 | 2.0 | 31 | 30 |
| | 1.0 | 15.0 | 5.0 | 30 | 29 |
| | 1.0 | 15.0 | 10.0 | 29 | 27 |
| | 1.0 | 15.0 | 0 | 2 | |
| | 1.0 | 15.0 | | | |

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Table 6

| Germicide | Amount added (part by weight) | Triethanol- | Triethanol- | Amount of diso- | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|--------------------------------------|----------------------------------|---------------------------|---------------|-----------------|--|--|
| | | amine lauryl phosphate | amine laurate | | | |
| Benzalkonium hexa- decylphosphate | 1.0 | 10.0 | 10.0 | 0.5 | 34 | 32 |
| | 1.0 | 10.0 | 10.0 | 1.0 | 35 | 32 |
| | 1.0 | 10.0 | 10.0 | 2.0 | 35 | 32 |
| | 1.0 | 10.0 | 10.0 | 5.0 | 36 | 33 |
| | 1.0 | 10.0 | 10.0 | 10.0 | 33 | 30 |
| | 1.0 | 10.0 | 10.0 | 0 | 2 | 1 |
| | 1.0 | 10.0 | 10.0 | | | |
| | 1.0 | 10.0 | 10.0 | | | |
| Benzalkonium chloride | 1.0 | 10.0 | 10.0 | 0.5 | 35 | 31 |
| | 1.0 | 10.0 | 10.0 | 1.0 | 36 | 31 |
| | 1.0 | 10.0 | 10.0 | 2.0 | 36 | 32 |
| | 1.0 | 10.0 | 10.0 | 5.0 | 36 | 30 |
| | 1.0 | 10.0 | 10.0 | 10.0 | 35 | 30 |
| | 1.0 | 10.0 | 10.0 | 0 | 2 | 2 |
| | 1.0 | 10.0 | 10.0 | | | |
| | 1.0 | 10.0 | 10.0 | | | |

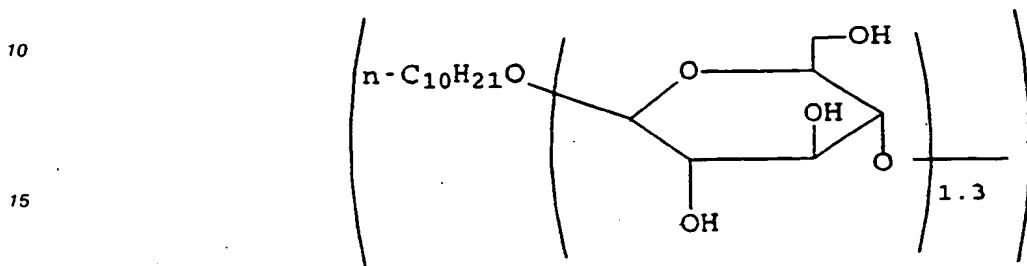
55 Examples 4:

The germicidal effects of various germicides (benzalkonium hexadecylphosphate, benzalkonium chloride, didecyldimethylammonium chloride and chlorhexidine gluconate) both in a system in which an anionic

surfactant and/or a nonionic surfactant was mixed with each germicide and in the case where a metal chelating agent was added to the mixed systems were investigated.

Method

5 The alkyl polyglycoside represented by the following formula (a nonionic surfactant) was mixed in a proportion of 10 parts by weight with 1 part by weight of each of the various germicides.



20 Portions of the resultant mixture were separately mixed with sodium EDTA as the metal chelating agent in varied proportions of 0.5-10.0 mols per mol of the germicide. Sterilized distilled water was added to each of the resulting mixtures to 100 parts by weight in total. As controls, systems to which the metal chelating agent, 3 parts by weight of triethanolamine laurate as the anionic surfactant or germicide was not added, and individual systems of these components, were prepared.

25 A germicidal test was performed in the following manner. Diluted systems of each mixture were prepared to inoculate each of germs (Escherichia coli IFO 3972 and Pseudomonas aeruginosa IFO 12689) to be tested in the systems to determine the concentration of the germicide necessary to completely kill the germs, and the time required to do so. More specifically, 0.1 ml of an SCD medium (product of Nippon Seiyaku K.K.) containing precultured germs (about 10^9 - 10^{10} cells/ml) was taken out and inoculated in 10 ml of the system diluted to the predetermined concentration (germicide concentration: 1, 5, 10, 25, 50, 75, 100, 200, 300 or 500 ppm) to conduct the test at room temperature. When predetermined periods of time (5, 10, 15 and 30 minutes) went on, a portion of the system inoculated with the germs was taken out by a platinum loop and inoculated in a micro Petri dish (96-cell wells, product of CORNING Co.) containing 0.3 ml of an SCD medium for after culture. Culture was conducted for 3 days at 30 °C to observe the growth of germs (by the naked eye), thereby judging the efficacy by the number of sterilized areas. More specifically, the judgment was made by counting areas (40 areas in the maximum number) where no germ grew on a microplanter.

35 The results are shown in Tables 7 and 8.

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Table 7

| Germicide | Amount added (part by weight) | Amount of alkyl polyglycoside added (part by weight) | Amount of tri- ethanolamine laurate added (part by weight) | Amount of chelating agent added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|---------------------------------------|-------------------------------------|--|---|---|--|--|
| Didecyldimethyl- ammonium chloride | 1.0 | 10 | 0 | 0.5 | 35 | 32 |
| | 1.0 | 10 | 0 | 1.0 | 39 | 33 |
| | 1.0 | 10 | 0 | 2.0 | 39 | 33 |
| | 1.0 | 10 | 0 | 5.0 | 38 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 38 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 36 | 30 |
| | 1.0 | 10 | 0 | 0 | 30 | 28 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |
| Chlorhexidine gluconate | 1.0 | 10 | 0 | 0.5 | 33 | 31 |
| | 1.0 | 10 | 0 | 1.0 | 35 | 32 |
| | 1.0 | 10 | 0 | 2.0 | 35 | 32 |
| | 1.0 | 10 | 0 | 5.0 | 34 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 34 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 34 | 30 |
| | 1.0 | 10 | 0 | 0 | 29 | 27 |
| | 1.0 | 10 | 3 | 0 | 0 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |

Table 8

| Germicide | Amount added (part by weight) | Amount of alkyl polyglycoside (part by weight) | Amount of tri- ethanolamine laurate (part by weight) | Amount of chelating agent added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|--------------------------------------|-------------------------------------|--|--|---|--|---|
| Benzalkonium hexa- decylphosphate | 1.0 | 10 | 0 | 0.5 | 33 | 30 |
| | 1.0 | 10 | 0 | 1.0 | 34 | 31 |
| | 1.0 | 10 | 0 | 2.0 | 34 | 31 |
| | 1.0 | 10 | 0 | 5.0 | 34 | 30 |
| | 1.0 | 10 | 3 | 1.0 | 33 | 30 |
| | 1.0 | 0 | 3 | 1.0 | 33 | 30 |
| | 1.0 | 10 | 0 | 0 | 31 | 28 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |
| Benzalkonium chloride | 1.0 | 10 | 0 | 0.5 | 35 | 30 |
| | 1.0 | 10 | 0 | 1.0 | 36 | 31 |
| | 1.0 | 10 | 0 | 2.0 | 37 | 32 |
| | 1.0 | 10 | 0 | 5.0 | 37 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 36 | 32 |
| | 1.0 | 0 | 3 | 1.0 | 35 | 31 |
| | 1.0 | 10 | 0 | 0 | 33 | 29 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 |
| | 0 | 10 | 0 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |

55 Examples 5:

The germicidal effects of various germicides (benzalkonium hexadecylphosphate, benzalkonium chloride, diidodecyltrimethylammonium chloride and chlorhexidine gluconate) both in a system in which an anionic

surfactant and/or a nonionic surfactant was mixed with each germicide and in a system in which a metal chelating agent was added to the mixtures were investigated.

A germicidal test was performed in the same manner as in Example 4 except that polyoxyethylene (3.0) lauryl ether was used instead of the alkyl polyglycoside as the nonionic surfactant.

The results are shown in Tables 9 and 10.

Table 9

| Germicide | Amount added (part by weight) | Amount of poly- oxyethylene (3.0) lauryl ether added (part by weight) | Amount of tri- ethanolamine laurate added (part by weight) | Amount of chela- ting agent added (mol) | Effect on E. coli (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) |
|---------------------------------------|-------------------------------------|---|---|---|--|---|
| Didecyldimethyl- ammonium chloride | 1.0 | 10 | 0 | 0.5 | 36 | 34 |
| | 1.0 | 10 | 0 | 1.0 | 37 | 34 |
| | 1.0 | 10 | 0 | 2.0 | 37 | 35 |
| | 1.0 | 10 | 0 | 5.0 | 38 | 35 |
| | 1.0 | 10 | 3 | 1.0 | 37 | 34 |
| | 1.0 | 0 | 3 | 1.0 | 37 | 34 |
| | 1.0 | 10 | 0 | 0 | 30 | 28 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 |
| | 0 | 10 | 0 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |
| Chlorhexidine gluconate | 1.0 | 10 | 0 | 0.5 | 32 | 30 |
| | 1.0 | 10 | 0 | 1.0 | 32 | 31 |
| | 1.0 | 10 | 0 | 2.0 | 33 | 31 |
| | 1.0 | 10 | 0 | 5.0 | 33 | 31 |
| | 1.0 | 10 | 3 | 1.0 | 32 | 30 |
| | 1.0 | 0 | 3 | 1.0 | 32 | 30 |
| | 1.0 | 10 | 0 | 0 | 29 | 27 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 |
| | 0 | 10 | 0 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |

Table 10

| Germicide | Amount added (part by weight) | Amount of poly- oxyethylene (3.0) lauryl ether added (part by weight) | Amount of tri- ethanolamine laurate added (part by weight) | Amount of chelating agent added (mol) | Effect on E. coli | | Effect on P. aeruginosa (number of sterilized areas) |
|----------------------------------|-------------------------------------|--|---|--|---------------------------------|---|---|
| | | | | | (number of sterilized areas) | Effect on P. aeruginosa (number of sterilized areas) | |
| Benzalkonium hexa-decylphosphate | 1.0 | 10 | 0 | 0.5 | 34 | 31 | 31 |
| | 1.0 | 10 | 0 | 1.0 | 34 | 31 | 31 |
| | 1.0 | 10 | 0 | 2.0 | 35 | 31 | 31 |
| | 1.0 | 10 | 0 | 5.0 | 35 | 32 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 34 | 31 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 34 | 30 | 30 |
| | 1.0 | 10 | 0 | 0 | 31 | 28 | 28 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 | 0 |
| Benzalkonium chloride | 1.0 | 10 | 0 | 0.5 | 35 | 31 | 31 |
| | 1.0 | 10 | 0 | 1.0 | 36 | 33 | 33 |
| | 1.0 | 10 | 0 | 2.0 | 36 | 33 | 33 |
| | 1.0 | 10 | 0 | 5.0 | 37 | 33 | 33 |
| | 1.0 | 10 | 3 | 1.0 | 35 | 31 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 35 | 31 | 31 |
| | 1.0 | 10 | 0 | 0 | 33 | 29 | 29 |
| | 1.0 | 10 | 3 | 0 | 1 | 0 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 | 0 |

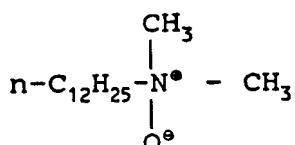
55 Example 6:

The germicidal effects of various germicides (benzalkonium chloride and chlorhexidine gluconate) both in a system in which an anionic surfactant and/or an amphoteric surfactant was mixed with each germicide

and in a system in which a metal chelating agent was added to such a system were investigated.

A germicidal test was performed in the same manner as in Example 4 except that alkyldimethylamine oxide represented by the following formula was used as the amphoteric surfactant instead of the alkyl polyglycoside as the nonionic surfactant.

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The results are shown in Table 11.

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Table 11

| Germicide | Amount added (part by weight) | Amount of alkyl- dimethylamine oxide added (part by weight) | Amount of tri- ethanolamine laurate added (part by weight) | Effect on E. coli (number of sterilized areas) | | Effect on P. aeruginosa (number of sterilized areas) |
|----------------------------|-------------------------------------|---|--|--|--|--|
| | | | | Amount of chelating agent added (mol) | Effect on E. coli (number of sterilized areas) | |
| Benzalkonium chloride | 1.0 | 10 | 0 | 0.5 | 35 | 31 |
| | 1.0 | 10 | 0 | 1.0 | 35 | 31 |
| | 1.0 | 10 | 0 | 2.0 | 36 | 31 |
| | 1.0 | 10 | 0 | 5.0 | 36 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 37 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 35 | 31 |
| | 1.0 | 10 | 0 | 0 | 30 | 27 |
| | 1.0 | 10 | 3 | 0 | 0 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |
| Chlorhexidine gluconate | 1.0 | 10 | 0 | 0.5 | 32 | 32 |
| | 1.0 | 10 | 0 | 1.0 | 33 | 32 |
| | 1.0 | 10 | 0 | 2.0 | 34 | 32 |
| | 1.0 | 10 | 0 | 5.0 | 34 | 32 |
| | 1.0 | 10 | 3 | 1.0 | 35 | 31 |
| | 1.0 | 0 | 3 | 1.0 | 34 | 31 |
| | 1.0 | 10 | 0 | 0 | 29 | 27 |
| | 1.0 | 10 | 3 | 0 | 0 | 0 |
| | 0 | 10 | 3 | 1.0 | 0 | 0 |
| | 0 | 10 | 0 | 0 | 0 | 0 |

As is apparent from Examples 1 to 6, it is understood that cationic germicides are greatly hindered in their inherent germicidal action when in the presence of an anionic surfactant and/or the like, while the germicidal action is not hindered when a metal chelating agent is added in at least preferably 0.5 mol per mol of the germicide to such a mixture. It is also understood that the compositions according to the present invention are useful compositions which satisfy both excellent germicidal power and detersity at the same

time.

The present application is based on Japanese Patent Applications No.5-205076 and No. 5-205077, both filed in Japan on August 19, 1993, which are incorporated herein in its entirety by reference.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Claims

- 10 1. A germicidal-disinfectant detergent composition comprising (a) a cationic germicide, (b) a metal chelating agent and (c) at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof,
wherein said metal chelating agent is present in an amount of at least 0.5 mole per mole of germicide.
- 15 2. The composition according to Claim 1, wherein the cationic germicide is selected from the group consisting of cationic surfactant germicides, biguanide germicides and amino acid germicides.
- 20 3. The composition according to Claim 1, wherein the metal chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid, hydroxyethylethylenediaminetriacetic acid, diethylenetriamine pentaacetic acid, nitrilotriacetic acid, triethylenetriamine hexaacetic acid, phosphonic acids, tripolyphosphoric acid, ethylene glycol-bis(2-aminoethyl ether)tetraacetic acid, citric acid, maleic acid, polyacrylic acid, isoamylene-maleic acid copolymers, silicic acid, gluconic acid, hydroxybenzylimidinoacetic acid, imidinoacetic acid, and salts of the said acids.
- 25 4. The composition according to Claim 1, wherein the anionic surfactant is selected from the group consisting of salts of higher fatty acids, salts of higher alcohol sulfates, salts of higher alcohol sulfonic acids, salts of sulfated fatty acids, salts of sulfonated fatty acids, salts of higher alcohol phosphates, salts of fatty acid ester sulfates, salts of fatty acid ester sulfonates, salts of higher alcohol ether sulfates, salts of higher alcohol ether sulfonates, salts of higher alcohol ether-substituted acetic acids, condensates of a fatty acid and an amino acid, salts of fatty acid amide alkylolated sulfates, salts of fatty acid amide alkylated sulfonates, salts of carboxymethyl-substituted ethoxylated fatty acid amides, salts of fatty acid sulfosuccinates, alkylbenzenesulfonates, alkylphenol sulfonates, alkylnaphthalenesulfonates and alkylbenzimidazolesulfonates.
- 30 5. The composition according to Claim 1, wherein the nonionic surfactant is selected from the group consisting of polyoxyethylene alkyl ethers, polyoxyethylene alkylene ethers, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbite fatty acid esters, alkyl polyglycosides, sucrose fatty acid esters and alkyl polyglycerol ethers.
- 35 6. The composition according to Claim 1, wherein the amphoteric surfactant is selected from the group consisting of alkyldimethyl-amino fatty acid betaines, alkyldimethylamine oxides and alkylcarboxymethylhydroxyethylimidazolium betaines.
- 40 7. The composition according to Claim 1, wherein the metal chelating agent is present in an amount of 0.5-5 mols per mol of the cationic germicide.
- 45 8. The composition according to Claim 1, which comprises (a) 0.1-10 wt.% of the cationic germicide, (b) 0.5-5 mols, per mol of the cationic germicide, of the metal chelating agent and (c) 1-80 wt.% of the surfactant.
- 50 9. The composition according to Claim 1, wherein the metal chelating agent is selected from ethylenediaminetetraacetic acid, hydroxyethylethylenediaminetriacetic acid, citric acid, tripolyphosphoric acid, and salts of the said acids.
- 55 10. A method for germicidal and disinfectant cleaning, which comprises the steps of cleaning a surface with a composition comprising (a) a cationic germicide, (b) a metal chelating agent present in a proportion of at least 0.5 mol per mol of the germicide and (c) at least one surfactant selected from anionic

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surfactants, nonionic surfactants and amphoteric surfactants.

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• Ikeda, Chikako
Wakayama-shi, Wakayama (JP)
• Okamoto, Juri
Wakayama-shi, Wakayama (JP)
• Tamura, Yoshinori
Wakayama-shi, Wakayama (JP)

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(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem. et
al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

(71) Applicant: KAO CORPORATION
Chuo-ku Tokyo (JP)

(72) Inventors:
• Hioki, Yuichi
Wakayama-shi, Wakayama (JP)
• Moriyama, Tadashi
Wakayama-shi, Wakayama (JP)

(54) Germicidal-disinfectant detergent composition

(57) A germicidal-disinfectant detergent composition comprising (a) a cationic germicide, (b) a metal chelating agent and (c) at least one surfactant selected from anionic surfactants, nonionic surfactants and amphoteric surfactants is described. Excellent detergency and germicidal action are provided.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 2457

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) | | | | | | |
|---|--|-------------------|---|-----------------|----------------------------------|----------|-----------|-----------------|-----------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | | | | | | | |
| X | WO-A-86 05509 (A. E. STALEY MANUFACTURING COMPANY) * page 6, line 5 - page 15, line 23; examples 1,2 * | 1-3,5, 7-10 | C11D3/48 A01N47/44 A01N33/12 | | | | | | |
| X | EP-A-0 478 445 (PETERS Z. I.) * page 2, line 48 - page 4, line 55 * | 1-3,5-10 | | | | | | | |
| X | EP-A-0 259 249 (CIBA-GEIGY AG) * page 2, line 34 - page 6, line 15; examples 1-26 * | 1,3-7,9 | | | | | | | |
| X | EP-A-0 175 338 (TAKEDA CHEMICAL INDUSTRIES LTD.) * page 3, line 5 - page 6, line 23 * | 1-3,7,9, 10 | | | | | | | |
| X | DE-A-34 45 901 (HENKEL KGAA) * page 6, paragraph 3 - page 11, paragraph 1; examples 1-5 * | 1-3,5-10 | | | | | | | |
| P,X | FR-A-2 695 297 (PETERS (S.A.)) * page 1, line 1 - page 7, line 18 * | 1-3,5-10 | TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D A01N | | | | | | |
| <p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; padding: 2px;">Place of search</td> <td style="width: 33%; padding: 2px;">Date of completion of the search</td> <td style="width: 33%; padding: 2px;">Examiner</td> </tr> <tr> <td style="padding: 2px;">THE HAGUE</td> <td style="padding: 2px;">23 January 1996</td> <td style="padding: 2px;">Doolan, G</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | | Place of search | Date of completion of the search | Examiner | THE HAGUE | 23 January 1996 | Doolan, G |
| Place of search | Date of completion of the search | Examiner | | | | | | | |
| THE HAGUE | 23 January 1996 | Doolan, G | | | | | | | |